EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

New Procedures for Uranium Isotope Ratio Measurements using the new TRITON Thermal Ionisation Mass Spectrometer

S. Richter, A. Alonso, H. Kühn, R. Wellum,
P.D.P. Taylor

Report EUR 21849

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Dr. Stephan Richter
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

E-mail: stephan.richter@cec.eu.int

Tel.: +32 (0)14 571-701, -652
Fax: +32 (0)14 571863

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

EUR Report
Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

New Procedures for Uranium Isotope Ratio Measurements using the new TRITON Thermal Ionisation Mass Spectrometer

S. Richter, A. Alonso, H. Kühn, R. Wellum,
P.D.P. Taylor

Abstract

In February 2004 the new Triton Thermal Ionization Mass Spectrometer from Thermo Electron has been installed at IRMM. For uranium isotope ratio measurements on the Triton at IRMM two basic techniques have been introduced and validated, namely the MTE- ("Modified Total Evaporation") and the HI- ("High Intensity") techniques. The performance of these techniques is considered excellent for uranium isotope ratio measurements to be performed at IRMM. Data obtained for the IRMM-183-187 series will be used to recertify the minor uranium ratios for these well known reference materials.

Introduction

The Triton thermal ionization mass spectrometer (TIMS) has been delivered to IRMM in December 2003, installed in January/February 2004 and accepted on February 12th, 2004.
The testing of the Triton has been primarily focused on uranium isotope measurements. Uranium isotope ratio measurements constitute one of most challenging tasks for a TIMS instrument because they cover a quite large dynamic range: the $^{235}U/^{238}U$ ("major") ratio ranges between ca. 0.002 and 1, and the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ("minor") ratios even range between 10^{-10} and 10^{-2}.
The test measurements were performed using the IRMM-183-187 series of reference materials. The test measurements basically included 2 methods for uranium measurements:

1.) MTE-Measurements ("MTE" = Modified Total Evaporation[1])

This method provides data for
- All major ratios $^{235}U/^{238}U$ (between ca. 0.002 and 1),
- Minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ between about 10^{-4} and 1 (using Faraday-collectors only).

2.) HI-Measurements ("HI" stands for high intensity)

This method provides the most precise data for
- All Minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ between about $2x10^{-5}$ and 1. (using Faraday-collectors only).
- All Minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ below about $2x10^{-5}$ (using the SEM ion counter).

This method does not provide reliable major ratio ($^{235}U/^{238}U$) data.

Both methods will be described in detail within the following two sections.

1.) MTE-Measurements ("MTE" = Modified Total Evaporation[1])

This measurement method was especially designed to take advantage of the Triton capabilities and is described in detail in [1]. Throughout the entire sample measurement time the evaporation is conducted on a block-by-block basis by a special pcl-script (pcl=process control language). The performance of a total evaporation measurement on a block-by-block basis rather than continuously allows the performance of inter-block actions such as e.g. inter-block-heating, peak-centering, ion beam focusing.
The result for the $^{235}U/^{238}U$ ratio is calculated similar to the "classical" total evaporation, which is given by the mean $^{235}U/^{238}U$ ratio for all mass cycles during the measurement time, weighed by the respective ^{238}U intensity (labelled *Int.(238U)*) of the same mass cycles:

$$\left(\frac{235U}{238U}\right)_{NBL-MOD-TE} = \frac{\sum_{cycles} Int.(235U)}{\sum_{cycles} Int.(238U)} = \frac{\sum_{cycles}\left(\frac{235U}{238U}\right)_{measured} Int.(238U)}{\sum_{cycles} Int.(238U)}$$

The minor isotopes ^{234}U and ^{236}U are detected only using the Faraday multi-collector by this method. The ^{234}U and ^{236}U intensities are corrected for tailing effects originated by the major isotope beams ^{235}U and ^{238}U. For each of the 5 mass cycles within each block the tailing effects are measured at masses 233.7 and 234.4 to provide an average tailing contribution at ^{234}U (mass=ca.234.05amu), and at masses 235.7 and 236.4, respectively, to provide an average tailing contribution at ^{236}U (mass=ca.236.05amu).

The mass cycle is arranged as follows:

Step	Cup L2	Cup L1	Cup C	Cup H1	Cup H2	Integration time (s)	Idle time (s)
1	234	235	236		238	32	2
2	233.7	234.7	235.7		237.7	16	14
3	234.4	235.4	236.4		238.4	16	2

Results for $^{235}U/^{238}U$ ratios for the IRMM-183-187 series of reference materials using the MTE method

Figure 1 shows the precision (external %RSD) for various methods to measure the $^{235}U/^{238}U$ ratio. The improvement in precision using the total evaporation technique is obvious for both the MAT 262 and the Triton.

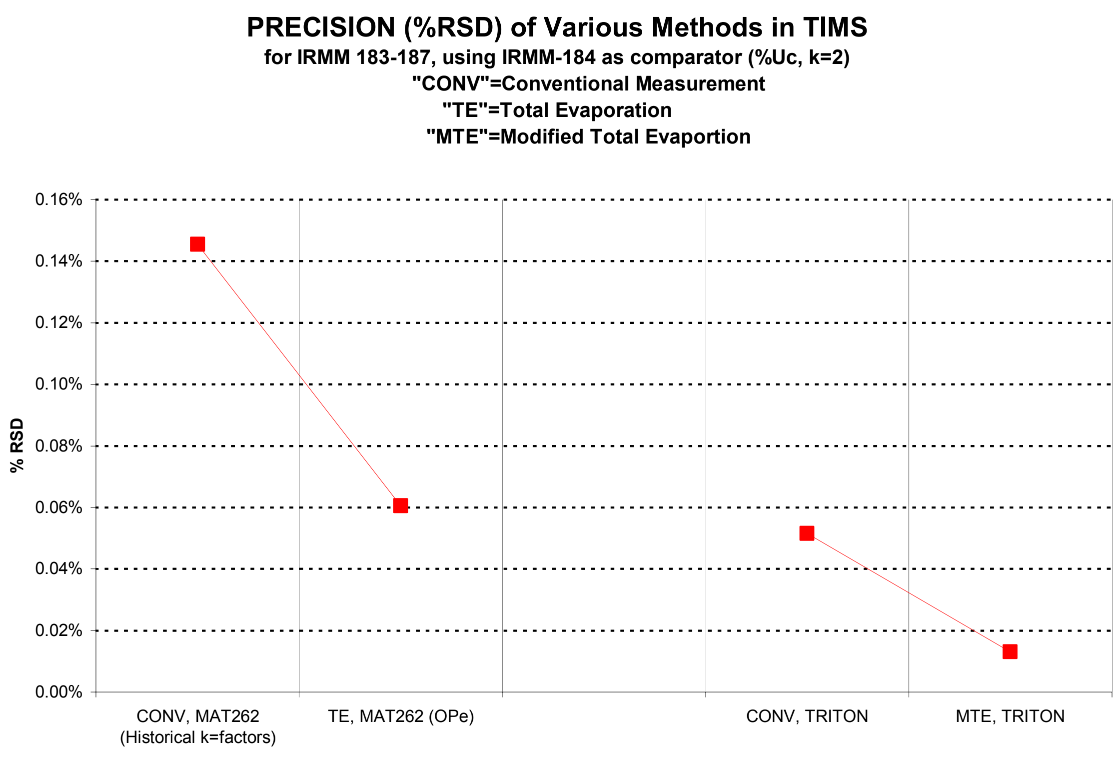


Fig. 1: Precision (%RSD) for various methods to measure the $^{235}U/^{238}U$ ratio. The precision of the MTE technique has been improved compared to data in [1] (in [1]: 0.025% RSD, now 0.015%RSD) due to changes in the heating pcl-script.

As stated in [1] a mass fractionation correction is required also for total evaporation measurements. Therefore, for a complete uncertainty statement, the measurement uncertainties of both the sample and the standard material (called “comparator” here) and also the stated uncertainty of the comparator on the certificate have to be included. The IRMM-184 was chosen as the comparator for this study because of its close to natural isotopic composition. But this choice is arbitrary; any other material could be chosen, assuming the fractionation is independent on the $^{235}U/^{238}U$ ratio. A typical uncertainty budget for the MTE-Triton measurement of IRMM-183 using IRMM-184 as comparator is given below. The uncertainty of the comparator on the certificate is the major source of uncertainty:

Parameter	Rel. Contribution to Comb. Uc
Ratio $^{235}U/^{238}U$ of sample (IRMM-183), uncorrected	13%
Ratio $^{235}U/^{238}U$ of comparator (IRMM-184), uncorrected	11%
Ratio $^{235}U/^{238}U$ of comparator (IRMM-184), as certified	74%

The combined uncertainties (k=2) for various methods are compared to each other in Figure 2. The typical combined uncertainty for the MTE method on the Triton is ca. 0.038%, which is quite similar to combined uncertainties obtained by the double standard method on the UF_6-gas mass spectrometer MAT511. Therefore the MTE and the UF_6-gas measurement techniques are complementary techniques for the determination of $^{235}U/^{238}U$ ratios for certification purposes.
The advantages of the MTE technique are:

- No memory effects have to be considered, one standard is sufficient for correction if the linearity of detection system has been proven (for Triton done at NBL, to be done at IRMM).
- Possibility to measure minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ between 10^{-4} and 1.

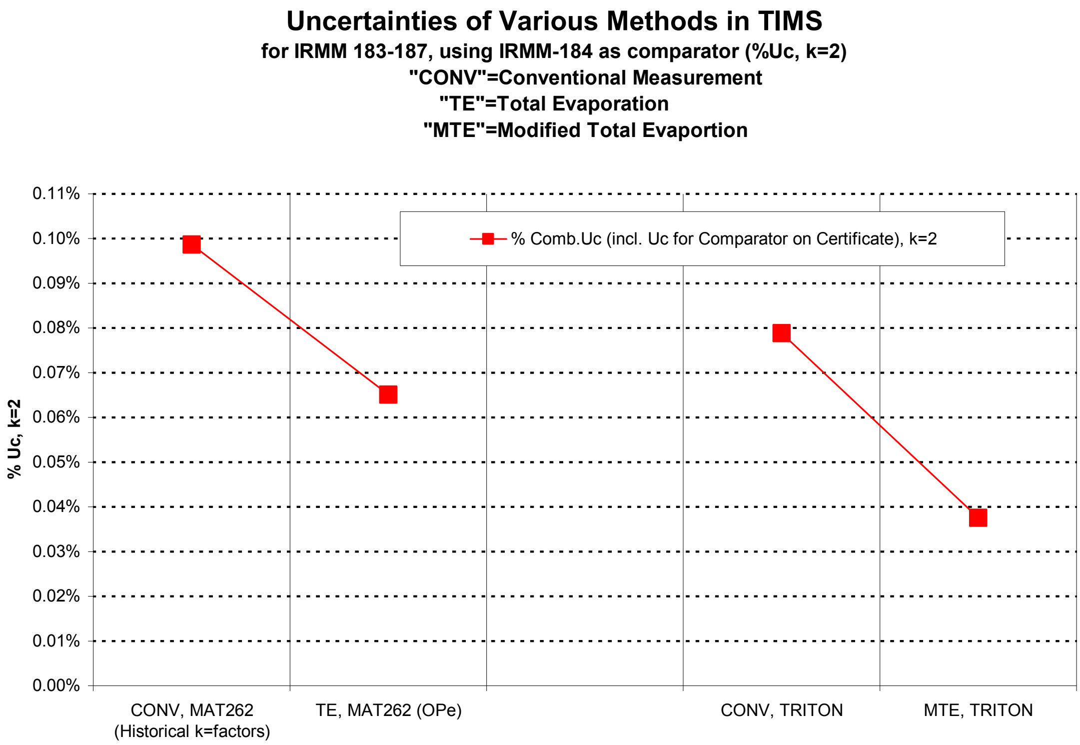


Fig. 2: Combined Uncertainties (k=2) for various methods to measure the $^{235}U/^{238}U$ ratio (for close to natural uranium, but dependency on the $^{235}U/^{238}U$ ratio has been observed on the Triton).

The results for $^{235}U/^{238}U$ for IRMM-183, IRMM-184, IRMM-185, IRMM-186 and IRMM-187 using various methods are plotted in Figure 3. Each data point reflects data for one magazine. The data are corrected using IRMM-184 as comparator. For

IRMM-183 there seems to be a significant deviation of the (corrected) ratio from the certified value. This has been confirmed in various experiments:

- MTE measurements on the Triton for 2 different ampoules of IRMM-183 (ampoule 1: magazines “MTE-3 Triton” and “CONV-3 Triton” and all MAT262 data, ampoule 1: magazines “MTE-4-5-6 Triton” and “CONV-4-5-6 Triton”).
- Conventional measurements on the Triton, they show higher uncertainties but indicate the same effect for IRMM183.
- Total Evaporation measurements on the MAT262, done by O. Pereira.

Conventional measurements on the MAT262 have large uncertainties and do not allow a conclusion for IRMM-183.

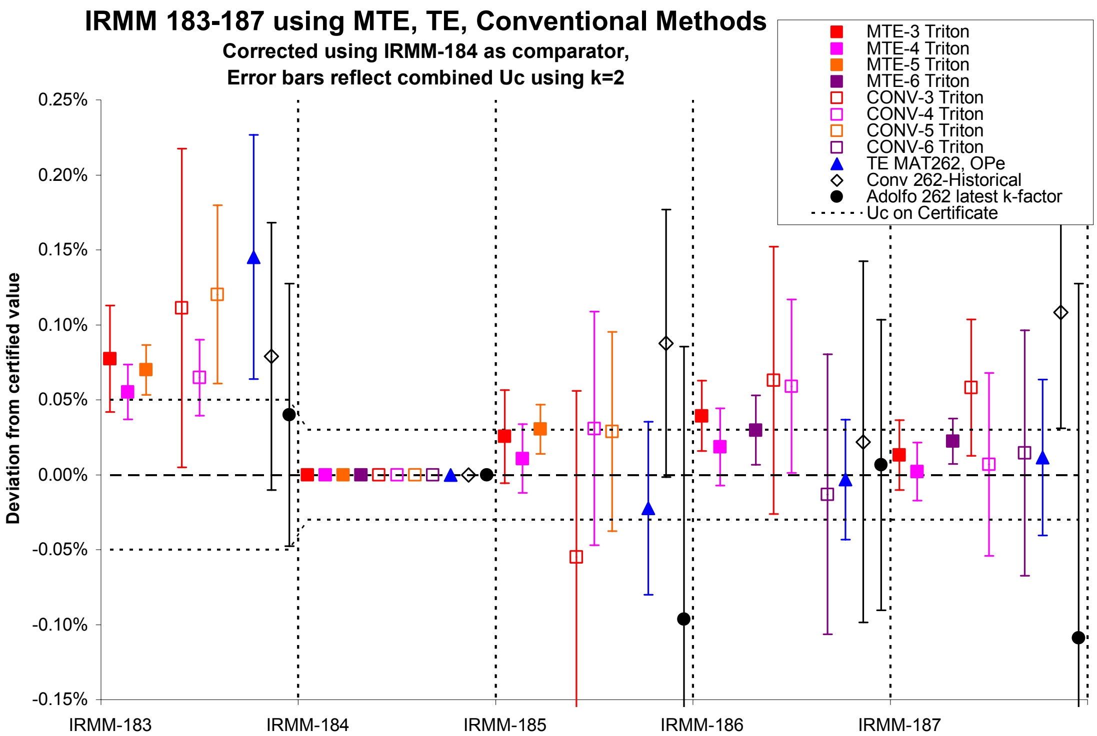


Fig. 3: Results for $^{235}U/^{238}U$ using the MTE and other techniques on the Triton and the MAT262. Each data point reflects data for one magazine.

Results for the MTE technique on the Triton (averages from magazines “MTE-3-4-5-6”) are tabulated below and shown in the following diagram.

	Ratio	Comb. Uc, k=2:	Rel. Comb. Uc, k=2:	Dev from Certified:
IRMM-183	0.0032179	0.0000011	0.035%	0.069%
IRMM-184	0.0072623			
IRMM-185	0.0200599	0.0000070	0.035%	0.024%
IRMM-186	0.030780	0.000011	0.035%	0.028%
IRMM-187	0.047331	0.000016	0.034%	0.013%

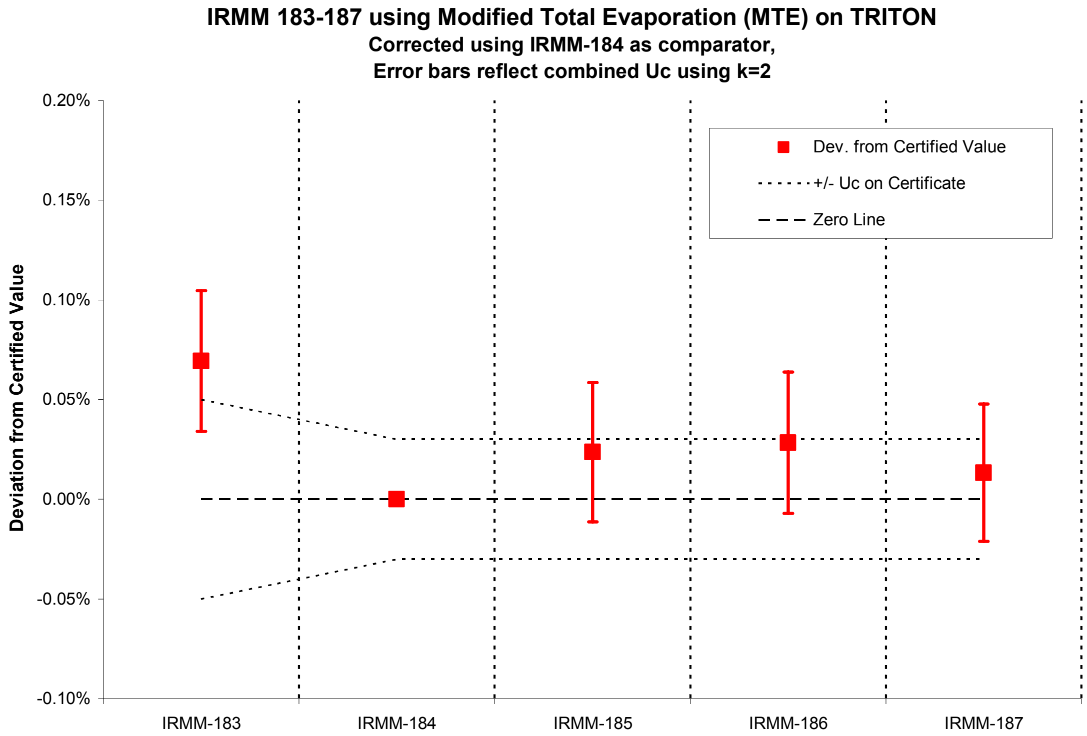


Fig. 4: Results for $^{235}U/^{238}U$ using the MTE technique on the Triton. Results using the other methods and the MAT262 (see Figure 1 and 2) were similar but showed higher uncertainties.

The deviation for IRMM-183 will trigger some further investigations, e.g. by comparison measurements on the UF_6-gas instrument.
The results for the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ between about $1x10^{-4}$ and 1 obtained during the MTE measurements on the Triton are presented together with the results of the HI-measurements in the following section.

Results for HI-Measurements ("HI" stands for high intensity)

This method provides the most precise data for

- All Minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ between about $2x10^{-5}$ and 1. (using Faraday-collectors only).
- All Minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ below about $2x10^{-5}$ (using the ion counter).

This method does not provide very reliable major ratio ($^{235}U/^{238}U$) data.

For HI-Measurements the filament temperatures/currents and ion beam intensities are adjusted to achieve the best possible precision and accuracy primarily for the minor ratios. Due to the special intensity requirements for HI-measurements samples with different major ratios $^{235}U/^{238}U$ may have to be measured at quite different ion beam intensities. Therefore a reliable determination of the major ratio is not possible, the major ratio of a given sample (e.g. measured at 25V for ^{238}U) cannot be corrected externally using a given standard which has been measured at a different ^{238}U intensity (e.g. 40V for ^{238}U).
During the course of the measurement major ratios are acquired as well, but they are used only for an internal mass fractionation correction, which is usually based on a known result from a UF_6-gas mass spectrometry measurement.
Minor ratio values in a range between about $2x10^{-5}$ and 1 can be measured using Faraday-collectors with the smallest uncertainty. For ratio values below $2x10^{-5}$ measurements using the ion counter provide smaller uncertainties. In the latter case the size of one "calibrating" ion beam has to be adjusted in a way that one isotope

beam has the size of 5 mV on the Faraday cup (±20%), which corresponds to ca. 300.000 cps (counts per second) on the ion counter. This “calibrating” ion beam can be either ^{235}U ^{234}U or ^{236}U. The use of ^{235}U for the calibration would cause quite low count rates on ^{234}U or ^{236}U and therefore large uncertainties. This method has been used successfully on the MAT262, where a calibration using of ^{234}U or ^{236}U is not possible. But due to the extended dynamic range of the Triton Faraday collectors (50V), the calibration can be done well using ^{234}U or ^{236}U. This requires ^{238}U ion beams of 30-40V. The results for the minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$ for IRMM-183-187 are tabulated below.

IRMM-183	234/238 on FAR	236/238 on FAR
Average	0.000019755	0.000148358
External SD (n>6)	0.000000024	0.000000036
External % RSD (n>6)	0.120%	0.024%
SE	0.000000011	0.000000016
RSE	0.054%	0.011%
Uc, k=2	0.000000025	0.000000059
Rel Uc, k=2	0.126%	0.040%
Uncertainty-Budget:		
Measurement, RSE	87.8%	22.7%
Fractionation correction	12.2%	77.3%
Certified value:	0.0000202	0.0001465
Uc, k=2	0.0000012	0.0000086
Rel Uc, k=2	6.0%	5.9%
Rel. Dev. Measured vs Certified	-2.0%	1.3%

IRMM-184	234/238 on FAR	236/238 on SEM
Average	0.000053155	0.00000012442
External SD (n>6)	0.000000034	0.00000000065
External % RSD (n>6)	0.064%	0.52%
SE	0.000000012	0.00000000023
RSE	0.023%	0.18%
Uc, k=2	0.000000032	0.00000000049
Rel Uc, k=2	0.060%	0.40%
Uncertainty-Budget:		
Measurement, RSE	56.0%	86.9%
Linearity correction [2]		6.4%
SEM/FAR calibration		6.4%
Fractionation correction	44.0%	0.3%
Certified value:	0.0000528	0.0000002
Uc, k=2	0.0000031	0.0000001
Rel Uc, k=2	5.9%	50.0%
Rel. Dev. Measured vs Certified	0.7%	-38.2%

IRMM-185	234/238 on FAR	236/238 on SEM
Average	0.000179498	0.0000028885
External SD (n>6)	0.000000101	0.0000000027
External % RSD (n>6)	0.056%	0.094%
SE	0.000000028	0.00000000111
RSE	0.016%	0.038%
Uc, k=2	0.000000091	0.00000000468
Rel Uc, k=2	0.051%	0.16%
Uncertainty-Budget:		
Measurement, RSE	37.6%	22.3%
Linearity correction [2]		38.1%
SEM/FAR calibration		38.1%
Fractionation correction	62.4%	1.5%
Certified value:	0.000176	0.00000286
Uc, k=2	0.000010	0.00000051
Rel Uc, k=2	5.7%	17.9%
Rel. Dev. Measured vs Certified	2.0%	1.1%

IRMM-186	234/238 on FAR	236/238 on SEM
Average	0.000293606	0.000033219
External SD (n>6)	0.000000080	0.000000015
External % RSD (n>6)	0.027%	0.047%
SE	0.000000023	0.000000006
RSE	0.008%	0.019%
Uc, k=2	0.000000126	0.00000004903
Rel Uc, k=2	0.043%	0.15%
Uncertainty-Budget:		
Measurement, RSE	13.5%	6.4%
Linearity correction [2]		45.9%
SEM/FAR calibration		45.9%
Fractionation correction	86.5%	1.8%
Certified value:	0.000289	0.0000336
Uc, k=2	0.000016	0.0000024
Rel Uc, k=2	5.7%	7.1%
Rel. Dev. Measured vs Certified	1.7%	-1.2%

This data set can be used for quality control in the future. For each magazine measured using the HI-technique some standard samples from the IRMM-183-187 series will be measured along with the samples to check the long-term performance of the Hi-technique.

IRMM-187	234/238 on FAR	236/238 on FAR
Average	0.000386996	0.000071965
External SD (n>6)	0.000000071	0.000000055
External % RSD (n>6)	0.018%	0.076%
SE	0.000000020	0.000000015
RSE	0.005%	0.021%
Uc, k=2	0.000000160	0.000000034
Rel Uc, k=2	0.041%	0.047%
Uncertainty-Budget:		
Measurement, RSE	6.0%	52.5%
Fractionation correction	94.0%	47.5%
Certified value:	0.0003803	0.0000720
Uc, k=2	0.000020	0.00000398
Rel Uc, k=2	5.2%	5.5%
Rel. Dev. Measured vs Certified	1.7%	-0.02%

The performance of the MTE- and HI-techniques for minor uranium isotope measurements is compared to other techniques in the following diagrams (Fig 5-6). Fig. 5 shows that the external % RSE (n=5 replicate measurements) of the MTE- and HI-technique at IRMM is slightly better (smaller) compared to NBL ([1]). The uncertainty including the mass fractionation correction using the certified value of the comparator standard is much higher for the U.S. standards (solid blue line compared to solid red line), only because the uncertainties of the $^{235}U/^{238}U$ ratios of those standards are higher.

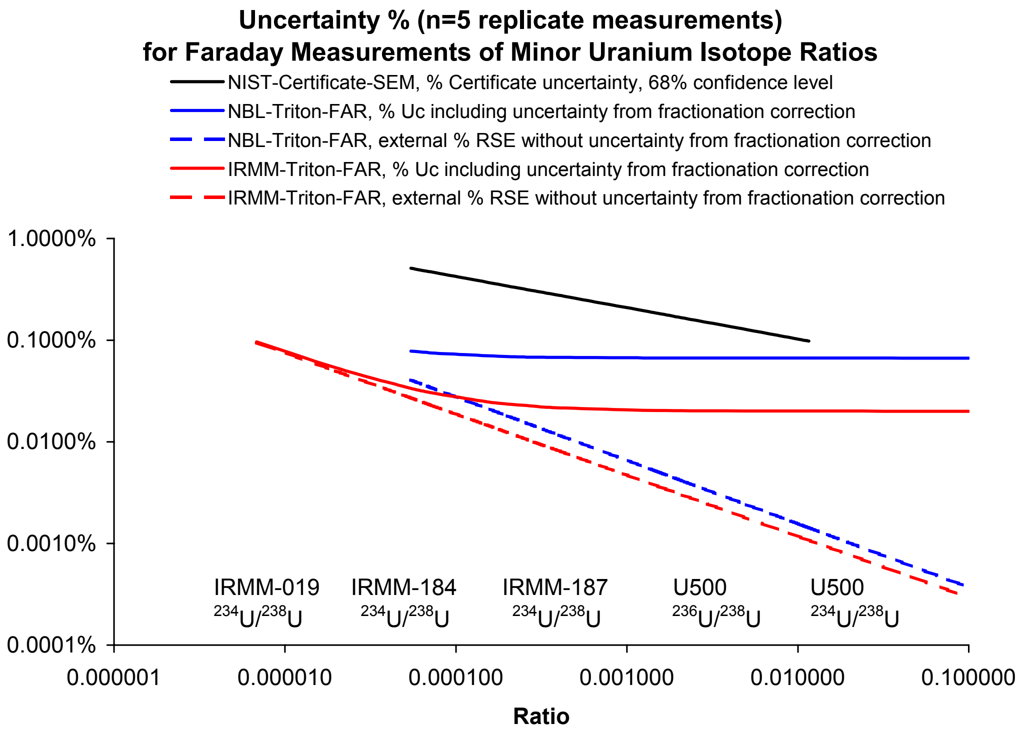


Fig. 5: Uncertainties for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ measurements using the MTE-technique on the Triton, compared with other techniques and the uncertainties of the certified values. All uncertainties are based on 5 replicate measurements (n=5). Increasing the number of replicates would move the left ends of the bold lines slightly down, but the right ends will stay the same.

Fig. 6 also includes the performance of HI-measurements using both the Faraday and the ion counter for some of the minor ratios at IRMM.

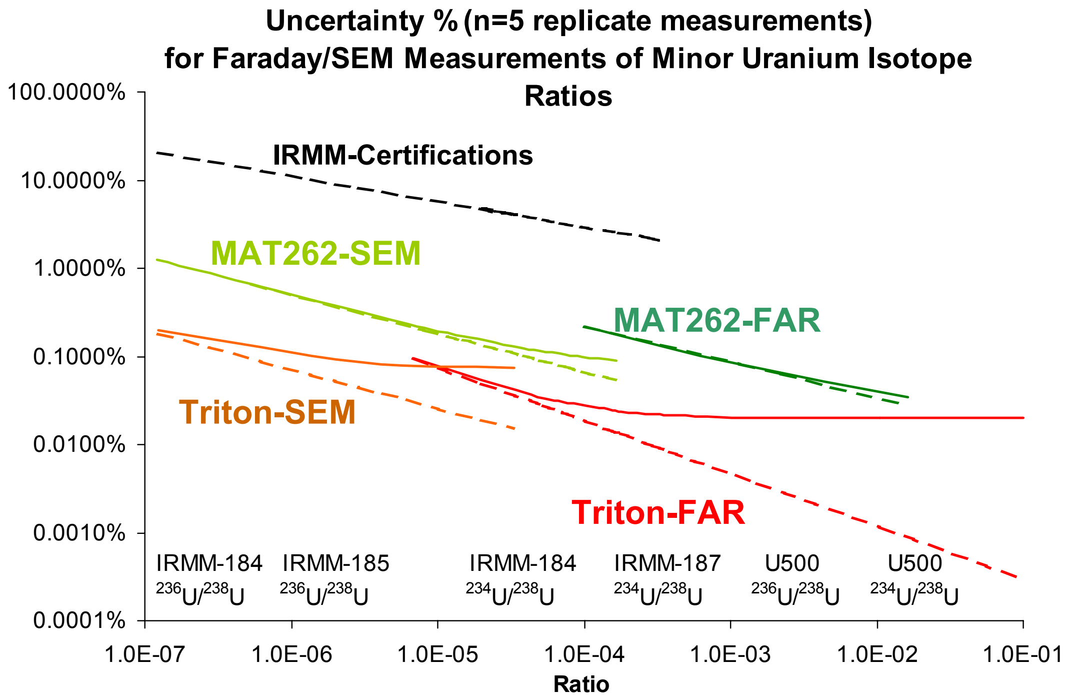


Fig. 6: Uncertainties for $^{234}U/^{238}U$ and $^{236}U/^{238}U$ measurements using the MTE- and HI-technique on the Triton, compared with other techniques and the uncertainties of the certified values. All solid lines include the uncertainty contribution from the mass fractionation correction; the dotted lines do not include this contribution.

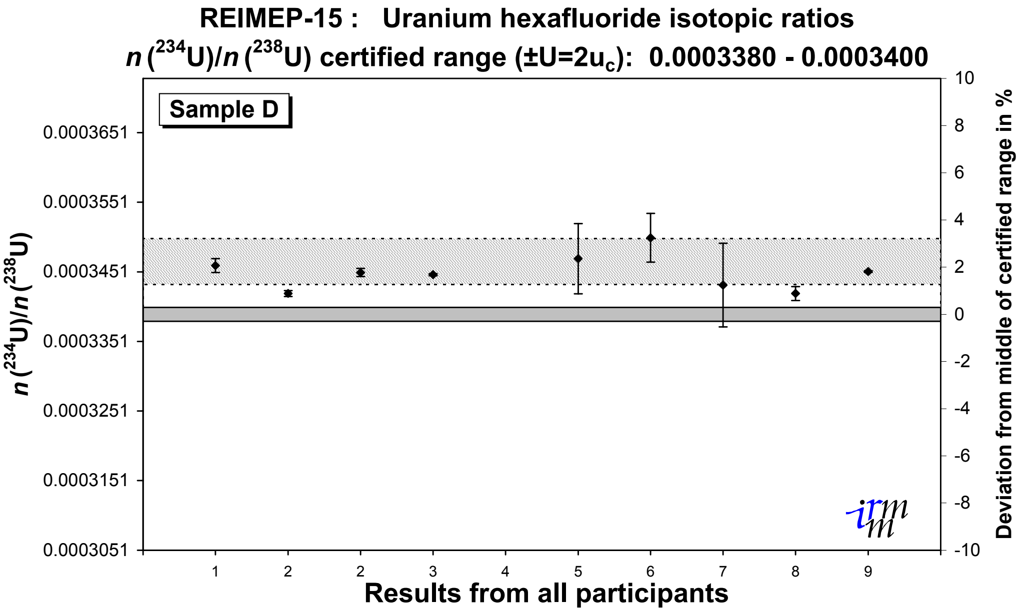
The improvement of the uncertainties over time due to instrumental developments is obvious. Starting with the uncertainties given on the certificates (in black), the uncertainties were first decreased by a factor of about 10 by using the MAT262 in Faraday mode and ion counting mode with ^{235}U as "calibrating" beam (green). The uncertainties were decreased by a factor of 10 again by using the Triton, either in Faraday mode (red) or in ion counting mode with ^{234}U as calibrating" beam (orange).
It is remarkable that the solid orange line (Triton-SEM) approaches the red orange line (Triton-FAR) at a ratio value of about $1x10^{-5}$. For ratios below this limit, Faraday measurements become more uncertain due to the unsatisfactory relationship between signal and noise. For those ratios a SEM measurement provides a lower uncertainty. For ratios higher than limit of $1x10^{-5}$, the reproducibility of SEM measurements might still become better (extrapolating the dotted orange line) but the combined uncertainty of SEM measurements is finally dominated by contributions arising from the mass fractionation, the linearity correction [2] and efficiency calibration for the SEM.

Conclusions:
For uranium isotope ratio measurements on the Triton at IRMM two basic techniques have been introduced, namely the MTE- ("Modified Total Evaporation") and the HI-("High Intensity") techniques. The performance of these techniques is similar compared to measurements at NBL and can be considered satisfactory for uranium isotope ratio measurements to be performed at IRMM. Data obtained for the IRMM-183-187 series will be used as reference for quality control on a regular basis. The new results can also be used to recertify the minor uranium ratios for the IRMM-183-187 materials.

Applications for the “HI” method:

A) REIMEP 15 Re-measurements:

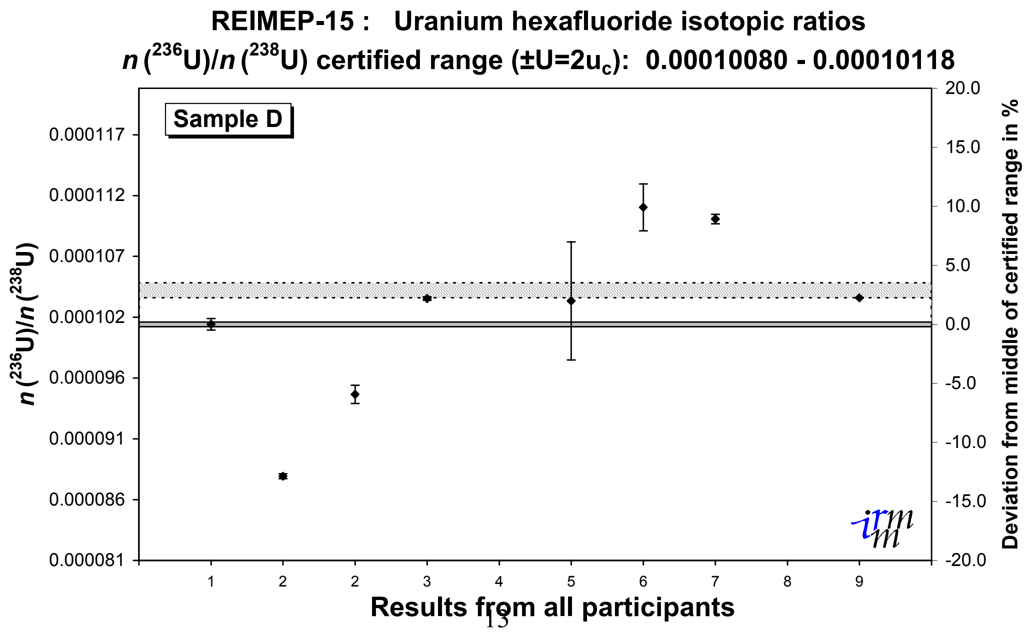
The materials of the REIMEP-15 campaign, samples A-D, have been re-measured using the “HI” method on the Triton for the minor isotope ratios. Those ratios have been previously certified using the MAT262 in ion counting mode for both ^{236}U and



^{234}U.

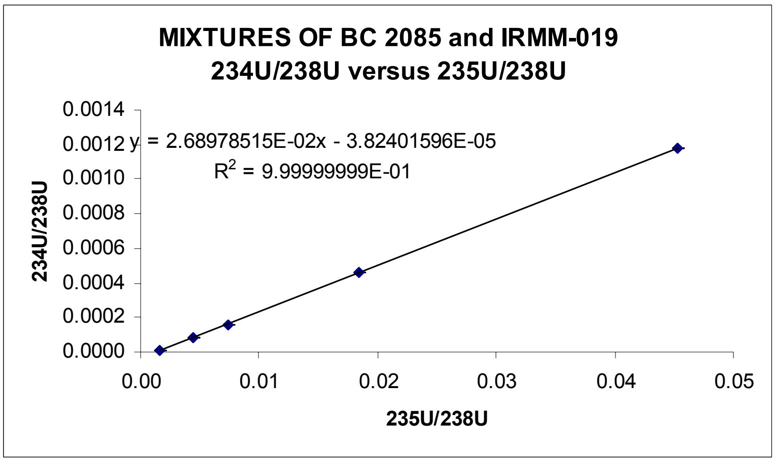
Fig. 7a,b: Results for REIMEP 15, sample D. The re-measured result using the Triton is added to the diagramm as #9.

Compared to the results from the majority of the participants those (old) certified data from IRMM showed some unresolved deviations. The deviations have now dissappeared in the current re-measurements. As an example, the results for REIMEP-15, sample D, are plotted in Fig.7a,b, where the new result is added to the diagramms as #9. The new data are in much better agreement with results from all other participants, especially for the $^{234}U/^{238}U$ ratio. The new data for the minor isotopes are suggested to replace the data on the current REIMEP 15 certificates.



B) Mixing of Uranium Samples with high ^{234}U and ^{236}U abundances:

A series of uranium isotope mixtures with relatively high ^{234}U and ^{236}U abundances (up to 0.1% and 1.6% respectively) has been prepared by W. De Bolle. The minor isotope abundances of these mixtures can be certified using the Faraday collector of the Triton. Therefore they are considered an ideal set of reference materials to calibrate the ion counting system of various types of isotope mass spectrometers.
The starting materials for the mixtures were BC 2085 and IRMM 019, the mixtures are labelled IRMM 3601-3603. The $^{235}U/^{238}U$ "major" ratios have been measured using the MAT511 UF_6-gas mass spectrometer, the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ "minor" ratios using the Triton (HI-method) in Faraday mode. Fig. 8a,b, show the mixing lines for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ "minor" ratios versus the $^{235}U/^{238}U$ "major" ratio.



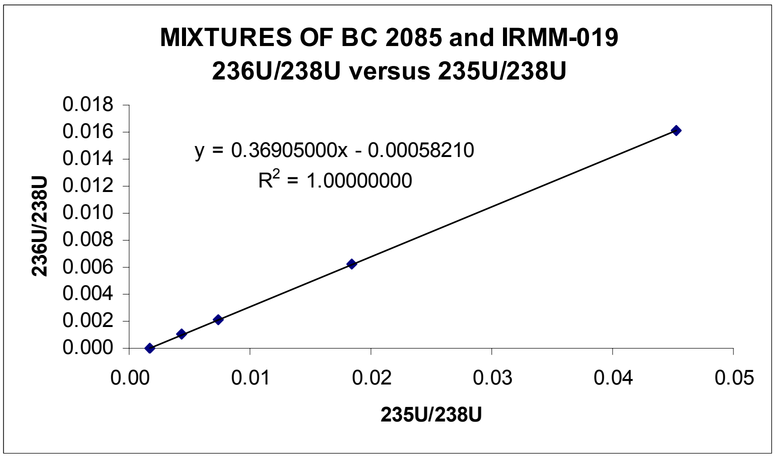
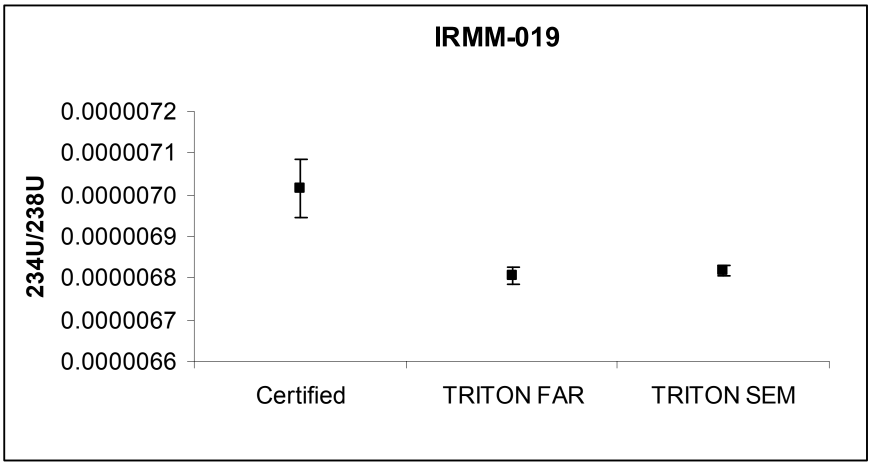


Fig. 8a,b: Mixing lines for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ "minor" ratios versus the $^{235}U/^{238}U$ "major" ratio.

It is remarkable that minor ratios such as $^{234}U/^{238}U$=0.000006807(21) and $^{236}U/^{238}U$=0.000036401(23) of IRMM-019 can be measured in Farday mode using the Triton. That would be impossible using the MAT262. The minor ratios of IRMM-019 have been confirmed in ion counting mode also.
Fig. 9a,b show a comparison of the certified ratios and the new data for IRMM-019. The Triton data in Faraday and ion counting mode agree with each other but they disagree significantly with the certified values. The reason might be an improper background correction for the tailing contribution from ^{238}U and ^{235}U in case of the certified ratios, but this assumption cannot be verified any more.



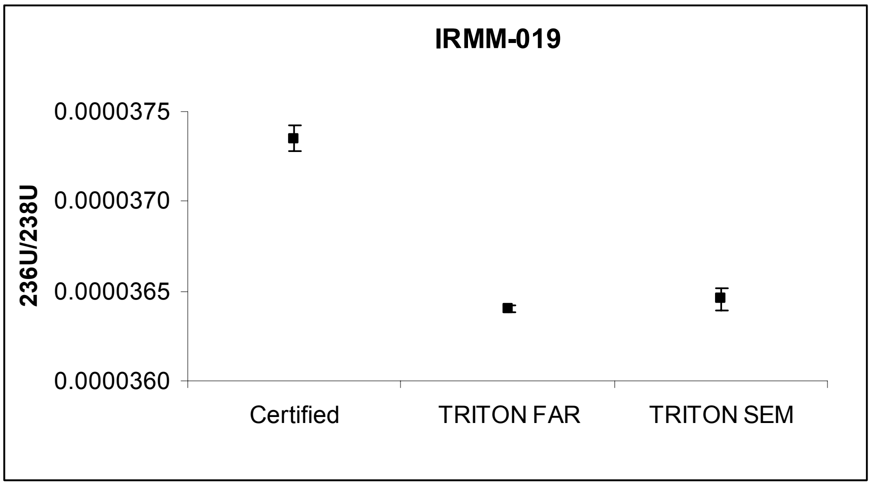


Fig. 9a,b: Results for minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$, comparison of certified ratios and remeasured results using the Triton in Faraday and ion counting mode.

All samples used for this mixing project (BC 2085, IRMM-3601-3603 and IRMM-019) are suggested to be re-certified for the minor ratios based on the new data obtained with the Triton.

As mentioned before the reference materials of the IRMM-183-187 series will be used for quality control measurements on a regular basis. Figure 10 shows the measured ratios for the $^{234}U/^{238}U$ ratio of IRMM-187 for the first 3-month period using the Triton.

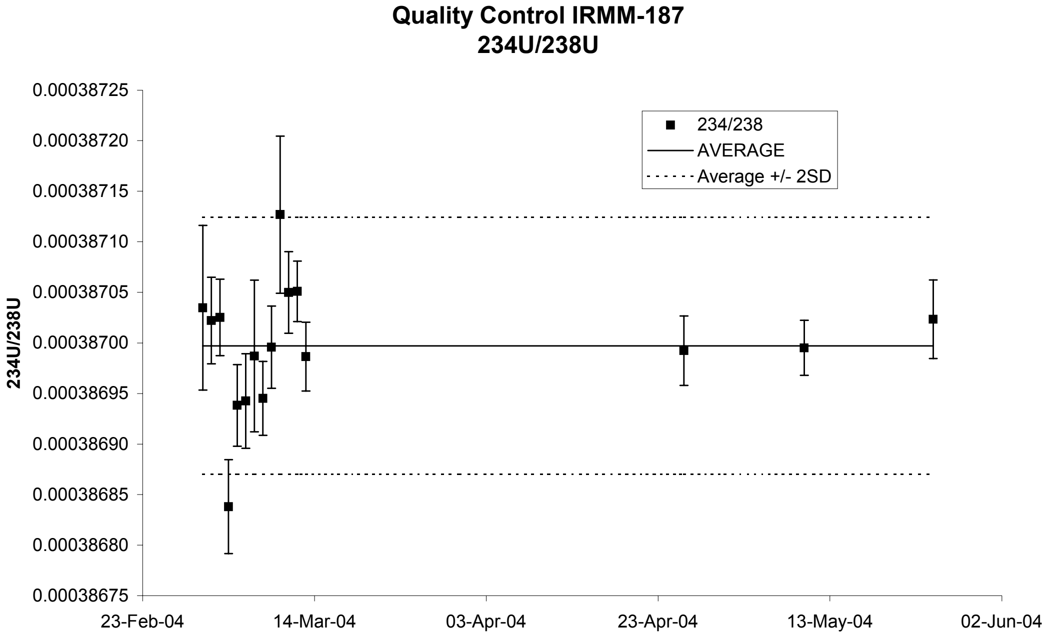


Fig. 10: Quality Control chart, examplary for the $^{234}U/^{238}U$ ratio of IRMM-187 for a 3 month period.

References:

[1] Richter, S., S. A. Goldberg (2003), Improved Techniques for High Accuracy Isotope Ratio Measurements of Nuclear Materials using Thermal Ionization Mass Spectrometry, International Journal of Mass Spectrometry, 229 (2003) 181-197.
[2] Richter, S., S. A. Goldberg, P. B. Mason, A. J. Traina and J. B. Schwieters (2001), Linearity Tests for Secondary Electron Multipliers Used in Isotope Ratio Mass Spectrometry, International Journal of Mass Spectrometry, 206/1-2, (2001) 105-127.

European Commission

EUR – DG Joint Research Centre, Institute for Reference Materials and Measurements –
Luxembourg: Office for Official Publications of the European Communities
2005 – 11 pp. – 21.0 x 29.7 cm
Scientific and Technical Research series

BACK COVER PAGE

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Community. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Publications Office
Publications.eu.int